CAAP Quarterly Report

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Contract Number: *DTPH5615HCAP02*

Prepared for: *US DOT - PHMSA*

Project Title: *"Understanding and Mitigating the Threat of AC Induced Corrosion on Buried Pipelines"*

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Business and Activity Section

(a) Generated Commitments –
Materials and supplies – chemicals, machine shop work to fabricate samples

(b) Status Update of Past Quarter Activities –

Summary:
We have made significant progress on three fronts this quarter: soil simulant, benchmarking of AC corrosion rates in simulant, and deposition of calcium carbonate films on pipeline steel. As discussed in our FY16 Q1 report, high soil resistivity is a problem for the small volumes of soil used in "soil box" type experiments. The high resistivity results in most of the potential (AC or DC) being dropped across the soil and not the electrochemical interface as desired. This is strictly a result of the small volumes used in the lab and not an issue for field studies on buried pipes. As such, we have chosen to use instead an aqueous soil simulant solution based on the chemical analysis of Ohio soils. Specifically, we are suing what is referred to as the NS4 soil simulant which consists of an aqueous solution containing: KCl=0.122 g/l, $NaHCO_3$=0.483 g/l, $CaCl_2.2H_2O$=0.181g/l and $MgSO_4.7H_2O$=0.131g/l. There are four different soil simulants (NS1-NS4) the composition of each approximates the chemical composition of different soils in North America. The soil analyses conducted in FY16 Q1 of this project indicate that the soil in northeast Ohio is best simulated by NS4. The use of these solutions is a well accepted practice in the corrosion research community (RN Parkins, *Corrosion Journal*, v. 50, 1994). Advantages of this method are decrease in solution resistance (increase in AC potential across electrochemical interface), ease of preparation and use.

With respect to benchmarking of AC corrosion rates in simulant, a senior undergraduate student (soon to be be employed by the pipeline industry), carried out a series of corrosion rate experiments on X65 steel in NS4 solution using the same parameters previously published by our group in sodium chloride solution (i.e.: AC potential, DC potential, AC frequency etc…). The student found that, as expected, the corrosion rates in NS4 were lower as compared to NaCl solution. However, the same trends with potential previously published for NaCl were also observed in NS4. Thus it is reasonable to conclude that the NS4 solution will provide a suitable electrochemical representation of the chemical constituents in Ohio soil. The student is currently writing up his results as part of his senior class design elective requirements.

Finally, we have made substantial progress on the deposition of calcium carbonate films on X65 steel. These films are meant to simulate those that might deposit on the surface of steel in Ca rich soils during long term exposure to cathodic protection (CP). In these experiments films on the order of $1x10^{-5}$ m thick were deposited onto X65 potentiostatically from a calcium rich solution. After the deposition process, the properties of these films were characterized extensively including film capacitance. It is proposed that one of the factors that contributes to the AC current passed at holiday is interfacial capacitance. If the AC current can be reduced, by changing the interfacial capacitance it may be possible to reduce corrosion rates due to AC currents. These samples are currently being exposed to 3V AC at 60Hz in NS4 at a CP potential of -0.85 V vs. copper sulfate electrode (CSE). Because the corrosion rates are so low at -0.85 V CSE, the exposure time for these experiments is approximately 1 month. Results will be reported in the third quarter progress report.

Experimental details:

- Preliminary electrochemical experiments in NS4 solution:
  - Performed potentiodynamic experiments without AC on API X65 carbon steel in NS4 solution.
  - Used data obtained from potentiodynamic results as input parameters for the theoretical model that were previously published for NaCl solution.

- AC corrosion experiments in NS4 solution:
  - Performed potentiostatic experiments at the same DC potentials of -720, -700, -670, -600, -500, -440, -600 and 0 mV vs. SCE with impressed AC potential as previous experiments in NaCl solution on API X65 carbon steel in NS4 solution.
  - Generated the RMS value of 600mV and 60 Hz using a Solartron 1255 FRA connected to the external input of the potentiostat.
  - Fitted values of interfacial capacitance for each experimental data point in the previously proposed theoretical model.
  - Compared experimental data of AC corrosion of X65 along with data obtained from the theoretical model in NS4 solution with those in NaCl solution.

- Deposition of calcium carbonate on X65 carbon steel:
  - Used solutions with different [Mg^{2+}] concentrations; ASTM norm D1141 artificial seawater and ASTM norm D1141 simulated sea solution with 0% [Mg^{2+}] concentration, to study the influence of Mg ions on the $CaCO_3$ layer deposition.
  - Used rotating disc electrode with different rpms to find the optimum rotation speed to obtain a uniform $CaCO_3$ layer.
  - Compared two different deposition procedures; potentiostaic and galvanostatic approaches, to get a homogenous carbonate layer on X65.
  - Performed in situ EIS analysis as calcareous deposits were forming on X65 at different time intervals to characterize the growth of calcium carbonate layers.
  - Performed SEM / FIB characterization of carbonate layers after deposition.
  - Performing a long term (30 days) potentiostatic experiments at cathodic protection potential (-0.85 $V_{Cu/CuSO4}$) with 3 V impressed AC potential on API X65 carbon steel with and without CaCO3 layer in NS4 solution.

Description of any Problems/Challenges –

- None to report

(c) Planned Activities for the Next Quarter –

- Iron (II) carbonate growth on API X65 carbon steel in carbon dioxide-saturated NaCl brine solution.
- Experimental and theoretical analysis and comparison of different scales grown on API X65 in NS4 soil simulant with applied AC and DC potentials.